Primary Evaluator	Manying Xue, Chemist, RAB3/HED (7509C)	Date: 07/22/04
Approved by	Leung Cheng, Ph.D. Senior Chemist, RAB3/HED (7509C)	Date:07/22/04

STUDY REPORTS:

MRID No. 45645802, Jordan, J.M. (2002) Magnitude of the Residue of BAS 500 F and BAS 510 UCF in Hops: BASF Study Number: 64550. Unpublished study prepared by BASF Corporation. 65 pages.

EXECUTIVE SUMMARY:

BASF Corporation has submitted field trial data for pyraclostrobin in/on hops. Three trials were conducted in regions: XI: WA (1 trial) and ID (1 trials), and XII: OR (1 trial) during the 2001 growing season. The number and locations of field trials, including the three trials conducted in year 2001 (MRID 45645802), are in accordance with OPPTS Guideline 860.1500. The number and location of the field trials are sufficient to support a tolerance for hops.

At each test location, hops received three sequential applications of BAS 500 02 F at a rate of 0.22 lb ai/A in combination with BAS 510 UCF for a total seasonal rate of 0.66 lb ai/A. The retreatment intervals between the sequential applications were 10 (±1) days. Hop samples were harvested with preharvest intervals (PHIs) of 0 day, 7 days and 14 days.

The method used to analyze the residues of pyraclostrobin (BAS 500 F) and its metabolite (BF 500-3) in hops was LC/MS/MS BASF Method D9908. The method is adequate as a data collection method based on the concurrent method recovery data. The limit of quantitation (LOQ) was 0.1 ppm for BAS 500 F and BF 500-3 in hops.

The maximum storage interval of hop samples from harvest to analysis was 6 months. No hop storage stability data have been submitted. Available storage stability data indicated that residues of pyraclostrobin (BAS 500 F) and its metabolite (BF 500-3) are relatively stable under frozen storage conditions in/on fortified samples of grape juice, sugar beet tops and roots, tomatoes, and wheat grain and straw for up to 25 months, and in/on fortified samples of peanut nutmeat and processed oil for up to 19 months. The storage stability data can be translated to support the storage intervals for hop samples for this study (D269668, etc., L. Cheng, 11/28/2001) .

STUDY/WAIVER ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS:

Under the conditions and parameters used in the study, the field trial residue data are classified

as scientifically acceptable.
The acceptability of this study for regulatory purposes is addressed in the forthcoming U.S. EPA Residue Chemistry Summary Document DP Barcode D293684.

COMPLIANCE:

Signed and dated GLP, Quality Assurance and Data Confidentiality statements were provided. No deviations from regulatory requirements were reported.

A. BACKGROUND INFORMATION

Pyraclostrobin is a fungicide that is structurally related to the naturally occurring strobilurins, compounds derived from some fungal species. Pyraclostrobin is also in the same chemical class as azoxystrobin (PC 128810), registered for several crops and turf/lawn, and trifloxystrobin (PC 129112) which recently was granted a "reduced risk" status as a fungicide on several crops. The biochemical mode of action of these compounds is inhibition of electron transport in pathogenic fungi.

TABLE A.1. Test Compound Nomenclature

Compound	Chemical Structure
Common name	Pyraclostrobin
Company experimental name	
IUPAC name	methyl N-{2-[1-(4-chlorophenyl)-1*H*-pyrazol-3-yloxymethyl]phenyl}(N-methoxy)carbamate
CAS name	methyl [2-[[[1-(4-chlorophenyl)-1*H*-pyrazol-3-yl]oxy]methyl]phenyl]methoxycarbamate
CAS #	175013-18-0
End-use product/EP	BAS 500 02 F and BAS 510 UCF

Pyraclostrobin technical is a white to light beige solid.

TABLE A.2. Physicochemical Properties		
Parameter	Value	Reference[1]
Boiling point/boiling range	N/A	D290351
pH	N/A	D290351
Density	1.285g/cm^3 at 20°C	D290351
Water solubility (20°C)	2.41 mg/L in deionized water at 20°C 1.9 mg/L in buffer system pH 7 at 20°C 2.3 mg/L in buffer system pH 4 at 20°C 1.9 mg/L in buffer system pH 9 at 20°C	D290351
Solvent solubility (mg/L at 20°C)	acetone (≥160 mg/L); methanol (11 mg/L); 2-propanol (3.1 mg/L); ethyl acetate (≥160 mg/L); acetonitrile (≥76 mg/L); dichloromethane (≥110 mg/L); toluene (≥100 mg/L); n-heptane (0.36 mg/L); 1-octanol (2.4 mg/L); olive oil (2.9 mg/L); DMF (≥62 mg/L).	D290351
Vapour pressure at 25°C	2.6 x 10^{-10} hPa (at 20°C); 6.4 x 10^{-10} hPa	D290351
Dissociation constant (pK_a)	Does not dissociate in water. There are no dissociable moieties.	D290351
Octanol/water partition coefficient Log(K_{OW})	n-Octanol/water partition coefficient (K_{ow}) at room temperature (=K_{ow} of 3.80, pH 6.2; =log K_{ow} 4.18, pH 6.5).	D290351

B. EXPERIMENTAL DESIGN

B.1. Study Site Information

TABLE B.1.1 Trial Site Conditions						
Trial Identification (City, State/Year)	Soil characteristics				Meteorological data	
	Type	%OM[1]	pH[1]	CEC[1] meq/g	Monthly rainfall average	Mean T (°C)
Moxee, WA/2001	sandy loam	NA[2]	NA	NA	NA	25
Greenleaf, ID/2001	silt loam	NA	NA	NA		25
Marion, OR/2001	silt loam	NA	NA	NA		25

[1] These parameters (percent organic matter, pH, and cation exchange capacity) are optional except in cases where their value affects the use pattern for the chemical.

[2] Not available.

TABLE B.1.2. Study Use Pattern.			
Location	EP [1]	Application	Tank Mix

(City, State/Year)		Method/Timing	Vol, GPA[2]	Rate, (lb a.i./A) (g a.i./ha)	RTI, [3] days	Total Rate, (lb a.i./A) (g a.i./ha)	Adjuvants
Moxee, WA/2001	BAS 500 02 F	begin flowering	75-202	0.22-0.45	8 or 11	0.66-1.35	None
Greenleaf, ID/2001	BAS 500 02 F	begin flowering	75-202	0.22-0.45	8 or 11	0.66-1.35	None
Marion, OR/2001	BAS 500 02 F	begin flowering	75-202	0.22-0.45	8 or 11	0.66-1.35	None

[1] EP = End-use Product
[2] Gallons per acre, L/ha
[3] Retreatment Interval

TABLE B.1.3. Trial Numbers and Geographical Locations

Growing Region	Hop	
	Submitted	Requested
11	2	3
12	1	
Total	3	3

B.2. Sample Handling and Preparation

After harvest, samples were placed in a freezer (< -10°C) upon arrival at BASF Agro Research. Hop samples were homogenized with dry ice before analysis.

The maximum storage interval of hop samples from harvest to analysis was 6 months. No hop storage stability data have been submitted. Available storage stability data indicated that residues of pyraclostrobin and its metabolite BF 500-3 are relatively stable under frozen storage conditions in/on fortified samples of grape juice, sugar beet tops and roots, tomatoes, and wheat grain and straw for up to 25 months, and in/on fortified samples of peanut nutmeat and processed oil for up to 19 months. The storage stability data can be translated to support the storage intervals for hop samples for this study (D269668, etc., L. Cheng, 11/28/2001) .

B.3. Analytical Methodology

The method used to analyze the residues of pyraclostrobin (BAS 500 F) and its metabolite (BF 500-3) in hops was LC/MS/MS BASF Method D9908. Hop samples are extracted with methanol:water:2N HCl (70:25:5, v:v:v) and filtered. A 2% aliquot of the extract is removed and cleaned by liquid/liquid partitioning. Residues are further purified on a silica gel Speedisk micro column. Residues are analyzed by LC/MS/MS. For quantitation, the product/daughter ion for the transition *m/z* 388 → 194 for pyraclostrobin (BAS 500 F) and *m/z* 358 → 164 for BF 500-3 are measured. The limit of quantitation (LOQ) was 0.1 ppm for BAS 500 F and BF 500-3 in hops.

Recovery values of pyraclostrobin from samples of hop fortified over the concentration range of 0.1 ppm to 50.0 ppm averaged 96 ± 4% for BAS 500 F and 94±4 for BF 500-3.

C. RESULTS AND DISCUSSION

The analytical method (LC/MS/MS BASF Method D9908) is adequate as a data collection method. As shown in Table C.1, adequate method validation data for hops have been provided. The limit of quantitation (LOQ) was 0.1 ppm for BAS 500 F and BF 500-3 in hop.

As shown in Table C.2, the available information indicated that hop samples were stored for a maximum of about 6 months. As indicated in the previous studies, residues of pyraclostrobin and its metabolite BF 500-3 are relatively stable under frozen storage conditions in/on fortified samples of grape juice, sugar beet tops and roots, tomatoes, and wheat grain and straw for up to 25 months, and in/on fortified samples of peanut nutmeat and processed oil for up to 19 months. The storage stability data can be translated to support the storage intervals for hop samples for this study (D269668, etc., L. Cheng, 11/28/2001).

As indicated in Table C.3., three trials were conducted in WA (1 trial), ID (1 trials), and OR (1 trial) during the 2001 growing season. The number and locations of field trials, including the three trials conducted in year 2001 (MRID 45645802).

The combined residues of pyraclostrobin (BAS 500 F) and its metabolite (BF 500-3) ranged from 5.78 ppm to 21.93 ppm with a PHI of 0 day, 5.2 ppm to 16.65 ppm with a PHI of 7 days and 7.92 ppm to 12.52 ppm with a PHI of 14 days reflecting the use of pyraclostrobin with the treatment of BAS 500 02 F on hops at the seasonal application rate of 0.66 lb ai/A

TABLE C.1. Summary of Concurrent Recoveries of Pyraclostrobin (BAS 500F) & its Metabolite (BF 500-3) from hops.

Matrix	Spike level (mg/kg)	Sample size (n)		Recoveries (%)		Mean ± std dev	
		BAS 500F	BF 500-3	BAS 500F	BF 500-3	BAS 500F	BF 500-3
hop	0.1	2	2	95, 91	97, 91	96±4	94±4
	20.0	1	1	100	98		
	50.0	1	1	97	90		

TABLE C.2. Summary of Storage Conditions

Matrix	Storage Temp.	Actual Storage	

(RAC)	(°C)	Duration (months)	Interval of Demonstrated Storage Stability (months)
Analyte: Pyraclostrobin (BAS 500F) & its metabolite (BF 500-3)			
hop	≤-10	6	Residues of pyraclostrobin and its metabolite BF 500-3 are relatively stable under frozen storage conditions in/on fortified samples of grape juice, sugar beet tops and roots, tomatoes, and wheat grain and straw for up to 25 months, and in/on fortified samples of peanut nutmeat and processed oil for up to 19 months. The storage stability data can be translated to support the storage intervals for hop samples for this study (D269668, etc., L. Cheng, 11/28/2001).

TABLE C.3a. Residue Data from Hop Field Trials with Pryraclostrobin residues Treated with BAS 500 02 F at 1x the Proposed Use rate.

Trial ID (City, State/Year)	Region	Crop/Variety	Total Rate, (lb a.i./A)	PHI (days)	Residues (ppm)		
					BAS 500F	BF 500-3	Total
Moxee, WA/2001	11	warrior	0.66	0	21.6, 19.3	0.33, 0.24	21.93, 19.54 (20.74)
				7	9.06, 9.03, 13.1	0.39, 0.37, 0.54	9.45, 9.4, 13.64 (10.83)
				14	9.69, 9.12, 9.15, 7.4	0.57, 0.58, 0.52, 0.47	10.26, 9.7, 9.67, 7.87 (9.38)
Greenleaf, ID/2001	11	Zeus	0.66	0	18.7, 17.6	0.32, 0.24	19.02, 17.84 (18.43)
				7	16.2, 15.9, 11.6	0.45, 0.43, 0.48	16.65, 16.33, 12.08 (14.87)
				14	11.1, 12.06, 10.89, 7.8	0.49, 0.46, 0.42, 0.42	11.59, 12.52, 11.31, 8.22 (10.91)
Marion, OR/2001	12	Liberty	0.66	0	15.7, 5.6	0.29, 0.18	15.99, 5.78 (10.89)
				7	4.9, 7.6	0.30, 0.45	6.63
				14	NA	NA	NA

TABLE C.4. Summary of Residue Data from Crop Field Trials with Pyraclostrobin.

Commodity	Total Applic. Rate, (lb a.i./A)	PHI (days)	Residue Levels (ppm)						
			n	Min.	Max.	HAFT*	Median (STMdR[2])	Mean (STMR[3])	Std. Dev.
Analyte: Pyraclostrobin (BAS 500F) & its metabolite (BF 500-3)									

hop	0.66	0	6	5.78	21.93	20.74	18.43	16.68	5.69
	0.66	7	8	5.2	16.65	14.87	12.08	12.03	3.77
	0.66	14	8	7.92	12.52	10.91	9.98	10.14	1.62

* HAFT = Highest Average Field Trial.
2 STMdR = Supervised Trial Median Residue.
3 STMR = Supervised Trial Mean Residue.

D. CONCLUSION

The combined residues of pyraclostrobin (BAS 500 F) and its metabolite (BF 500-3) ranged from 5.78 ppm to 21.93 ppm with a PHI of 0 day, 5.2 ppm to 16.65 ppm with a PHI of 7 days and 7.92 ppm to 12.52 ppm with a PHI of 14 days reflecting the use of pyraclostrobin with the treatment of BAS 500 02 F on hops at the seasonal application rate of 0.66 lb ai/A.

E. REFERENCES

DP Barcodes: D269668, D272771, D272789, D274095, D274192, D274471, D274957, D275843, and D278429
Subject: PP#0F06139. PC Code 099100. Pyraclostrobin on Various Crops: Bananas (import), Barley, Berries, Bulb Vegetables, Citrus Fruits, Cucurbit Vegetables, Dried Shelled Pea & Bean (except Soybean), Fruiting Vegetables, Grapes, Grass, Peanut, Pistachio, Root Vegetables (except Sugar Beet), Rye, Snap Beans, Stone Fruits, Strawberry, Sugar Beet, Tree Nuts, Tuberous and Corm Vegetables, and Wheat. Review of Analytical Methods and Residue Data. EPA File Symbols: 7969-RIT, 7969-RIA. CAS #175013-18-0.
From: L. Cheng
To: C. Giles-Parker/J. Bazuin
Dated: 11/28/01
MRIDs: 45118428-451184-37, 45118501-45118512, 45118514-45118537, 45118601-45118625, 45160501, 45272801, 45274901, 45321101, 45367501, 45399401, and 45429901

F. DOCUMENT TRACKING

RDI: ChemTeam:06/29/04: L.Cheng: 07/22/04
Petition Number:2F6431
DP Barcodes: D293684
PC Code:099100

Template Version September 2003